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A Solution Concentration Model for Carbon-in-Pulp Simulation

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ABSTRACT

This article describes a procedure for carbon-in-pulp (CIP) simulation based on a dual mass-transfer kinetic approach. The method attempts to overcome the short-comings of frequently used single-rate simulation techniques and at the same time, addresses the mathematical complexities of multirate modeling procedures.

Operating parameters for a full-scale CIP plant were utilized to test the new simulation approach. It was found that this simplified approach, based entirely on solution concentration, provided a significant improvement on certain current single-rate expression models.

Key Words: Activated carbon; CIP; Solution concentration; Mass-transfer kinetics.

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INTRODUCTION

Activated carbon has found increasing application with CIP technology in the gold mining sector. The efficient use of charcoal as an adsorbent to recover aurocyanide from solution has led to the replacement of the historical zinc precipitation technique by CIP technology at most gold mines around the world. This increased use of activated carbon has led to many research projects with the aim of understanding this adsorption phenomenon. This has not only resulted in a better understanding of the process, but has also resulted in various modeling procedures.[1–3]

Adsorption onto solid surfaces from solution is not well understood.[4,5] However, it is generally believed that gold adsorption onto activated carbon follows a dual kinetic rate, i.e., film diffusion and intraparticle diffusion. Thus, simplified models based on a single rate expression[1,2] may lead to significant errors, especially in stages where carbon loading exceeds 60% of total capacity.[6,7] Furthermore, models that attempted to address this shortcoming[3] are mathematically complex and difficult to apply to continuous processes.[6] These models are usually based on some form of resistance modeling, incorporating both film transport and intraparticle diffusivity. The difficulty in applying these models is the result of the assumption that equilibrium exists at the solid–liquid interface. Hence, numerous iterations are required using search algorithms during a simulation. Furthermore, these models are based on sound theoretical principles but rely heavily on equilibrium isotherms, usually of an empirical nature, which do not describe equilibrium conditions well over wide concentration limits.[8] Recently a thermodynamical model based on Metropolis Monte Carlo simulation was developed to overcome the shortcomings of frequently used equilibrium isotherms.[9,10] This method provides improved equilibrium predictions but does not address the numerous iterations required when applying a resistance model. Furthermore, the rate of intraparticle diffusivity is not constant and should be subdivided into diffusion into the macro-, meso- and micropores of the carbon, resulting in a relatively large number of parameters that must be solved.[3,6] Finally, it has been shown that the rate of diffusion is not constant and is influenced by solution concentration adding to the difficulty in applying resistance modeling.[11]

During the late 1990s, the need for a simplified, yet accurate, simulation procedure for CIP operations was probably as important as in the early years of CIP utilization. This is ascribed to the decreasing dollar gold price and ever-increasing mining costs. Gold producers under this economic pressure had to find means, such as increased throughput and lower head grades, for sustained economic viability. Thus, operating variables had to be continuously adjusted at no or little capital cost, hence, the need for simplified and accurate predictions.

In this study, the over simplification of a single rate expression is addressed by utilizing a solution concentration model (SCM) in which carbon loading has an indirect effect on mass-transfer kinetics. Also, mathematical simplicity is applied although a dual kinetic rate is acknowledged.

EXPERIMENTAL

Batch experiments were conducted in 1-L baffled tank reactors, agitation provided by a flat blade impeller at 200 rpm. The pH of the solutions was constant at 10.9. Aurocyanide of an analytical grade was used with solution concentration measured by an atomic absorption spectrophotometer. ANK-11, coconut shell carbon was used, with carbon loading determined by mass balance.

All continuous CIP findings are based on full-scale production data. The plant consists of 8 tanks each with a volume of 346 m^3. The feed rate was 413 $t{\cdot}h^{-1}$ at a relative density of 1.45 containing 2.2 $g{\cdot}t^{-1}$ dissolved gold. Regenerated carbon had an approximate loading of 90 $g{\cdot}t^{-1}$ with the average carbon transfer rate 0.5 $t{\cdot}h^{-1}$.

MODELING

CIP modeling is usually based on a concentration gradient where the difference between the gold in solution and that on the carbon provides the driving force for the process. However, when studying a solution concentration decay diagram of batch adsorption data, it becomes apparent that a large section of the profile yields a constant rate of adsorption at various carbon loadings. This implies that identical mass-transfer kinetics is achieved at various carbon loadings. What makes the concentration gradient approach even more susceptible to errors is the fact that a constant rate of gold adsorption is achieved at increasing carbon loading and reducing solution concentration values. This fact led to the idea that solution concentration is the main driving force and that carbon loading has an indirect effect on adsorption rate.

Hypothesis

- Solution concentration is the main mass-transfer driving force given normal CIP operating variables.
- Adsorption kinetics is a linear function of solution concentration if the ratio $\frac{S}{C}$ is larger than a certain critical value (external diffusion control).
- Adsorption kinetics is a logarithmic function of solution concentration once the critical ratio has been reached (internal diffusion control).
- The carbon loading in a stage is adequately described by using an average value.
- The effect of back-mixing is negligible.

It must be noted that the first assumption is based on the general philosophy that CIP circuits do not operate near equilibrium conditions where a model based on solution concentration alone may result in significant errors.

Formulas

$$\text{rate} = f(S) \ \text{ if } \ \frac{S}{C} > \text{critical} \tag{1}$$

and

$$\text{rate} = f(\ln S) \ \text{ if } \ \frac{S}{C} < \text{critical} \tag{2}$$

A mass balance over reactor i yields:

$$F_s(S_{i-1} - S_i) = F_c(C_i - C_{i+1}) = \text{rate of gold recovery} \tag{3}$$

$$F_c(C_i - C_{i+1}) = M_c\, k_c\, S_i \tag{4}$$

or

$$F_c(C_i - C_{i+1}) = M_c(k_d \ln S_i + A) \tag{5}$$

Hence, by rearrangement

$$S_i = \frac{F_c(C_i - C_{i+1})}{M_c k_c} \ \text{ if } \ \frac{S_i}{C_i} > \text{critical} \tag{6}$$

$$S_i = \exp\left[\frac{\left(\frac{F_c(C_i - C_{i+1})}{M_c} - A\right)}{k_d}\right] \ \text{ if } \ \frac{S_i}{C_i} < \text{critical} \tag{7}$$

RESULTS AND DISCUSSION

Batch Experiments

The assumptions made were tested by performing three batch experiments. The critical values of the three experiments were estimated from visual inspection of the profiles with the following obtained:

Batch1:	0.0017
Batch2:	0.0021
Batch3:	0.0024
Average:	0.0021

Batch operations are very different to continuous CIP operations. No solution or carbon is transferred while solution concentration decay occurs until equilibrium is reached. Hence, the solution decay profile may be estimated by the following:

$$\frac{\Delta S}{\Delta t} = k_c S \ \ if \ \ \frac{S}{C} > critical \tag{8}$$

$$\frac{\Delta S}{\Delta t} = k_d \ln(S) + A \ \ if \ \ \frac{S}{C} < critical \tag{9}$$

By selecting a 1-sec time increment, the k_c, k_d, and A values were obtained without difficulty by trial and error and evaluated to $0.00023\,s^{-1}$, $0.002\,s^{-1}$, and $0.0001\,mg{\cdot}l^{-1}{\cdot}s^{-1}$ respectively. The experimental results, together with the model predictions, are tabulated and graphically illustrated in Table 1 and Fig. 1 respectively. The resulting small average percentage errors obtained indicates a good model correlation with experimental results.

Continuous CIP Results

Randomly selected monthly average data listed in Table 2 were utilized with the corresponding gold adsorption rates calculated by mass balance.

The SCM model was evaluated against two other commonly used simplified models rather than against fundamental models, which are not often used in the simulation of CIP plants due to the complexities mentioned previously.

Table 1. Experimental and model results for batch experimentation.

Time (minute)	Batch 1 (mg/l)	Model 1 (mg/l)	Batch 2 (mg/l)	Model 2 (mg/l)	Batch 3 (mg/l)	Model 3 (mg/l)
0	5.1	—	6.8	—	10.2	—
10	4.6	4.4	5.4	5.9	8.5	8.9
20	4.0	3.9	5.0	5.2	8.2	7.7
30	3.7	3.4	4.6	4.6	7.6	6.9
60	3.0	2.8	3.8	3.9	6.0	6.0
120	2.0	1.9	2.5	2.7	4.7	4.5
180	1.2	1.2	1.6	1.7	3.4	3.1
240	0.8	0.9	1.1	1.1	2.6	2.1
300	0.6	0.7	0.6	0.8	2.0	1.4
Average % error per reference point		6.2		8.8		10.4

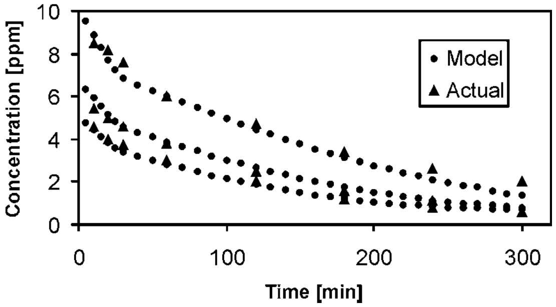

Figure 1. Model predictions for batch experimentation.

The kn Model

This model[1] suggests the following:

$$\frac{S_F}{S_i} = \left[1 + k\left(\frac{M_c}{F_c}\right)^n \times \frac{F_c}{F_s}\right]^i \tag{10}$$

By mathematical manipulation, the relationship can be linearized to obtain estimates of k and n.

Table 2. Data utilized for continuous CIP simulation.

Tank number	S $(\mathrm{mg}\cdot\ell^{-1})$	C $(\mathrm{g}\cdot\mathrm{t}^{-1})$	M_c (t)	Rate $(\mathrm{g}\cdot\mathrm{h}^{-1})$
1	1.35	2719	4.6	680
2	0.86	1360	3.9	368
3	0.21	624	3.4	129
4	0.12	366	4.2	49
5	0.04	275	3.7	32
6	0.02	211	4.2	28
7	0.01	155	4.0	18
8	0.01	119	3.7	15

$$\ln\left[\frac{\left(\frac{S_f}{S_i}\right)^{\frac{1}{i}}-1}{\frac{F_c}{F_s}}\right] = n\ln\left(\frac{M_c}{F_c}\right) + \ln k \tag{11}$$

The relevant plot is shown in Fig. 2 and indicates a weak linear fit with k and n evaluating to $21{,}375\mathrm{h}^{-1}$ and -1.5, respectively. This result is unexpected since the range for k and n is reported to be in the ranges 60 to 200 and 0.7 to 1.0, respectively.[5]

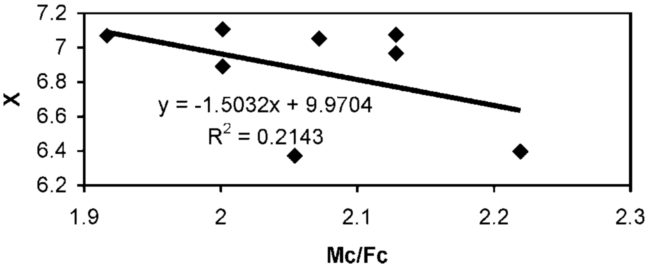

Figure 2. Linearized kn plot.

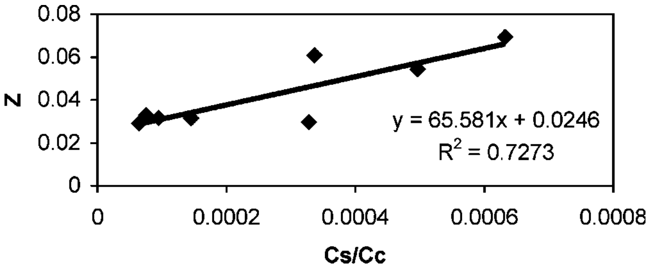

Figure 3. Linearized updated kn plot.

Undated kn Model

This model is of the following form[2]:

$$C_i = \frac{C_{i+1} + KS_i k\left(\frac{M_c}{F_c}\right)}{1 + k\left(\frac{M_c}{F_c}\right)} \tag{12}$$

By rearrangement, the following is obtained:

$$\frac{\mathrm{C_i} - \mathrm{C_{i+1}}}{\left(\frac{\mathrm{M_c}}{\mathrm{F_c}}\right)\mathrm{C_i}} = \mathrm{kK}\frac{\mathrm{S_i}}{\mathrm{C_i}} - \mathrm{k} \tag{13}$$

The resulting linear plot is shown in Fig. 3, which indicates an improved fit when compared to the kn model. However, the k and K values obtained are both negative at $-0.025\,\mathrm{h}^{-1}$ and -2624, respectively. The negative rate

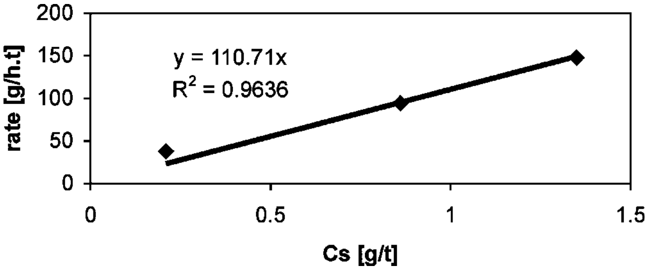

Figure 4. Rate vs solution concentration above critical value applied to plant data.

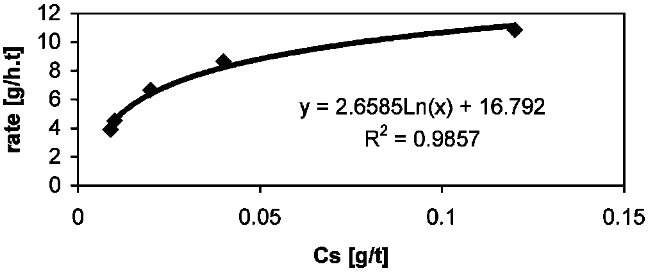

Figure 5. Rate vs solution concentration below critical value applied to plant data.

constant indicates a dominant reverse reaction for all stages, which is clearly not the case.

SCM

Figures 4 and 5 show the result of applying a critical value of 0.0003 to the model. The linear trend at $\frac{S}{C} >$ critical and logarithmic trend at $\frac{S}{C} <$ critical is clearly detected. The k_c, k_d, and K values evaluates to 110.7 h^{-1}, 2.7 h^{-1}, and 16.8 $gt^{-1}h^{-1}$, respectively.

Table 3. Predicted solution concentrations for plant CIP operation.

Tank number	Actual S ($mg{\cdot}\ell^{-1}$)	S (k_n) ($mg{\cdot}\ell^{-1}$)	S (updated k_n) ($mg{\cdot}\ell^{-1}$)	S (SCM) ($mg{\cdot}\ell^{-1}$)
1	1.35	1.22	1.22	1.33
2	0.86	0.55	0.92	0.85
3	0.21	0.20	0.34	0.34
4	0.12	0.17	0.03	0.11
5	0.04	0.06	0.03	0.05
6	0.02	0.05	0.02	0.02
7	0.01	0.02	0.01	0.01
8	0.01	0.01	0.01	0.01
Σ abs(error)		0.56	0.43	0.18
Σ $(error)^2$		0.12	0.05	0.018

The critical value obtained from plant data is different to that obtained from the laboratory batch experiments. This result is not surprising since various factors, including agitation rate, slurry density, viscosity, the type of carbon used, ionic strength, pH, and dissolved O_2 levels, will influence the value of the critical constant. Hence, each system will have a unique critical constant.

A comparative summary between the models solution concentration predictions and actual data are listed in Table 3.

From Table 3, it is clear that the SCM provides more accurate predictions than the other two simplified single-rate models. This is manifested by the significant lower values obtained for the sum of errors and sum of errors squared. However, the data was generated from a low-grade CIP plant. It is not suggested that the SCM model will necessarily outperform the two other models under consideration at higher feed concentrations.

CONCLUSION

It was found that an adsorption model based on solution concentration and a critical value can be accurate for CIP simulation purposes. This model outperformed other simplified single-rate modeling procedures when applied to low-grade data. However, this approach must be tested for higher grade data to establish the accuracy of predictions under varying solution values.

NOMENCLATURE

A = constant ($g \cdot t^{-1} \cdot h^{-1}$ or $mg \cdot l^{-1} \cdot s^{-1}$ for batch experiments)
C = carbon loading ($g \cdot t^{-1}$)
F = feed rate ($t \cdot h^{-1}$)
k = rate constant (h^{-1} or s^{-1} for batch experiments)
K = equilibrium parameter (unitless)
M = mass (t)
n = constant
S = solution concentration ($mg \cdot \ell^{-1}$)
X = $\dfrac{\left(\dfrac{S_F}{S_i}\right)^{\frac{1}{i}} - 1}{\dfrac{F_c}{F_s}}$
Z = $\dfrac{C_i - C_{i+1}}{\left(\dfrac{M_c}{F_c}\right)_{C_i}} (h^{-1})$

Subscripts

c = carbon or constant rate
d = diminishing rate
F = feed
i = tank number
s = solution

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